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## Description

## Background of the Invention

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The present invention relates to a sizing agent for use in cellulosic paper-making.

Heretofore a wide variety of sizing agents for use in paper-making have been proposed such as rosin-based, wax-based, alkylketene dimer based, polymer based, alkenylsuccinic anhydride based ones and the like and they have all been actually employed commercially. Since many of these conventional  
10 sizing agents are inherently water-insoluble, it is impossible to use them alone as such so it is usually necessary to disperse and/or emulsify them in water with the aid of an emulsifying agent. However, the emulsifying operation has such drawbacks that it is only achieved with difficulty and that said operation requires additional costs therefor.

The alkenylsuccinic anhydride based sizing agents in particular undergo hydrolysis with time due to their inherent nature if they are kept in contact with water for a short period of time, thereby losing their  
15 sizing effect.

Due to the poor stability in water of said alkenylsuccinic anhydrides based sizing agents, they have the serious limitation that the sizing treatment should be finished in a short period of time and this has been the greatest drawback for applying them commercially, in spite of such excellent effects that they  
20 exert adequate sizing effect in lower concentrations, thus providing greater economical benefits as compared to that of resin based, alkylketene dimer based, wax based sizing agents and the like.

The inventer has carried out a wide variety of investigations on the sizing effect of alkenylsuccinic acids and their derivatives having various structures, and as a result he has found that unsaturated hydrocarbyl partial esters of alkenylsuccinic acids and the salts thereof are at least self-emulsifiable with  
25 water and provide an excellent sizing effect.

For example, unsaturated hydrocarbyl diesters of alkenylsuccinic acids not only entail significant difficulties in their synthesis but they also require troublesome procedures for emulsifying similar to conventional sizing agents and further they require additional auxiliaries such as an activator. In addition, they are inferior to unsaturated monohydrocarbyl esters in sizing effect, which makes them useless  
30 commercially.

Further, saturated partial(mono)- and di- hydrocarbyl esters of alkenylsuccinic acids have substantially no sizing effect, thus they can not be used as a sizing agent. This is due to the fact that saturated hydrocarbyl mono- and di-esters of alkenylsuccinic acids are not substantially absorbed by paper and also they can only impart poor repellancy to paper. Contrary to the saturated hydrocarbyl mono- or di-  
35 esters, alkenylsuccinic anhydrides per se are readily absorbed by paper and make the resultant paper water repellent thereby exhibiting a sizing effect. However, once the anhydrides have been hydrolyzed to the corresponding dicarboxylic acids, the resulting dicarboxylic acids are not readily absorbed thus losing their sizing effect. In this way, alkenylsuccinic anhydrides have drawbacks in that they drastically change their identity in water with time thereby requiring adequate care.

He has also found that if unsaturated hydrocarbyl partial esters of alkenylsuccinic acids of the water-soluble salt thereof are employed in combination with an acid catalyst, a further improved sizing effect  
40 can be obtained.

## Summary of the Invention.

The object of the present invention is to provide a sizing agent which is at least self-emulsifiable and  
45 stable in water for a long period of time and which is effective in lower concentration.

Another object of the present invention is to provide a sizing agent which can be prepared without any difficulties.

Further objects of the present invention will become apparent from the description hereinafter referred to.

Thus, the present invention relates to a method of sizing paper utilizing as a sizing agent a composition  
50 comprising one or more partial esters of alkenylsuccinic acids represented by the formula:



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and/or one or more salts thereof, wherein R represents an unsaturated hydrocarbyl group having at least 6 carbon atoms and R' represents an unsaturated hydrocarbyl group having 3 to 18 carbon atoms.

The present invention further relates to use of a sizing agent as set out above, in combination with an  
60 acid catalyst.

## Detailed Description of the Invention.

It was generally known that compounds having unsaturated group or groups are strongly absorbed by paper and render the paper more hydrophobic than saturated compounds. The sizing agent of the present invention supports the above fact. Therefore, in contrast to saturated esters of alkenylsuccin-  
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ic acids which are only poorly absorbed by paper, thus having no sizing effect, unsaturated hydrocarbyl partial esters of alkenylsuccinic acids have surprisingly been found to be strongly absorbed by paper, making the paper significantly water-repellant, thereby providing an excellent sizing effect along with the advantages that they are not hydrolyzed by water, so that they can maintain their identity as a stable solution or dispersion in water for a long period of time. The unsaturated hydrocarbyl partial esters of alkenylsuccinic acids not only exhibit strong absorbability towards paper, but they also show no discoloring, and indicate a sustained stable sizing effect over a long period of time. Moreover, the unsaturated hydrocarbyl partial esters of the present invention provide consistently stable sized paper sheets even if said paper is treated with the agent in a low concentration.

The alkenylsuccinic anhydride or corresponding acid employed comprises all the alkenylsuccinic acid or anhydride in which the substituting side chain contains six or more than six carbon atoms and these include, for example, hexenyl-, octenyl-, decenyl-, octadecenyl-, dococenyl-, triancotenyl-, eicocenyl-, succinic acid and the like and corresponding anhydrides. As the unsaturated alcohols, there may be mentioned all the unsaturated alcohols having 3 to 18 carbon atoms such as allyl-, propargyl-, butenyl-, butyn-, pentenyl-, hexenyl-, octenyl-, decenyl-, laurenyl-, oleyl- alcohols and the like.

The unsaturated partial esters of the present invention can be converted to water-soluble products or at least self-emulsifiable products by converting the remaining free carboxyl group into a salt with alkaline metals or water-soluble amine whereby a stable aqueous solution or dispersion can be obtained by adding it to water. Upon use, it is preferable to use it with a cationic starch, an alkyleneoxide adduct based activator and the like as is conventionally employed in the art to fully assure the benefit of the sizing agent, although such use of an activator is not essential.

The unsaturated hydrocarbyl partial esters of alkenylsuccinic acids can be easily synthesized by a conventional esterification technique. Thus, an alkenylsuccinic anhydride or the corresponding acids and unsaturated alcohol are heated together to cause a reaction between them in the presence or absence of a catalyst through a ring opening in the case of anhydride, while in the case of acid through a dehydration to form an unsaturated partial ester. The ratio between the acidic starting material to the unsaturated alcohol is such that the amount of the alcohol is sufficient to esterify only one of the carboxyl groups of the acid.

The unsaturated hydrocarbyl partial esters of alkenylsuccinic acids of the present invention may be added to paper material in an amount of 0.0001 to 10 parts by weight per 100 parts by weight of paper material (dry base) and preferably 0.01 to 2.0 parts by weight per 100 parts by weight of paper material.

The use of the above catalyst can significantly reduce the amount of unsaturated hydrocarbyl partial ester and thus provide great economical advantages.

Although this increase in the sizing effect achievable by the use of acid catalyst cannot be fully understood at present, the following assumption may be induced, although this should not be regarded as binding to any particular theory. The acid catalyst such as the sulfonic acid, organic phosphoric acid, inorganic acid or Lewis acid excites the unsaturated linkage in the unsaturated hydrocarbyl partial esters, thereby bringing about a state where the double or triple unsaturated bond can be readily broken, so as to promote the etherification reaction with hydroxyl groups contained in cellulose or the esterification reaction by dehydration and that as a result the fixing of the sizing agent to paper is more fully effected in a short period of time.

As the acid catalyst, there may be mentioned sulfonic acid, organic phosphoric acid, inorganic acid, such as phosphoric acid, phosphorous acid, hypophosphorous acid, sulfuric acid, nitric acid, hydrochloric acid or the like, a Lewis acid such as boron fluoride, zinc chloride, aluminium chloride, ferric chloride and the like. These acid catalysts can be used alone or two or more in combination.

Among the sulfonic acid catalysts are included benzenesulfonic acid, toluene sulfonic acid, dimethylbenzene sulfonic acid, ethylbenzene sulfonic acid, diethylbenzene sulfonic acid, triethylbenzene sulfonic acid, styrene sulfonic acid, dichlorobenzene sulfonic acid, dichlorotoluene sulfonic acid, aniline sulfonic acid, aminotoluene sulfonic acid, dimethylaniline sulfonic acid, diaminobenzene sulfonic acid, diaminitoluene sulfonic acid, aniline disulfonic acid, anilinetrisulfonic acid, diaminobenzene disulfonic acid, ethyltoluidine sulfonic acid, diethylaniline sulfonic acid, chloroaniline sulfonic acid, aminochlorotoluene sulfonic acid, dichloroaniline sulfonic acid, nitrobenzenesulfonic acid, nitrotoluene sulfonic acid, dinitrobenzene sulfonic acid, dinitrostyrene sulfonic acid, nitrochlorobenzene sulfonic acid, chloronitrotoluene sulfonic acid, dinitrochlorobenzene sulfonic acid, nitroaniline sulfonic acid, phenylhydrazine sulfonic acid, methylphenylhydrazine sulfonic acid, phenol sulfonic acid, cresolsulfonic acid, dihydroxybenzene sulfonic acid, methacryloxybenzene sulfonic acid, aminophenol sulfonic acid, aminomethoxybenzene sulfonic acid, dimethoxyaniline sulfonic acid, chloroaminohydroxybenzene sulfonic acid, nitroaminohydroxybenzene sulfonic acid, butylbenzene sulfonic acid, naphthalene sulfonic acid, naphthalene disulfonic acid, methylnaphthyl sulfonic acid, ethylnaphthyl sulfonic acid, propylnaphthyl sulfonic acid, butylnaphthyl sulfonic acid, lignin sulfonic acid, naphthalene disulfonic acid, naphthalene trisulfonic acid, naphthylamine sulfonic acid, naphthylaminedisulfonic acid, naphthylamine trisulfonic acid, nitronaphthalene sulfonic acid, nitronaphthalene disulfonic acid, nitronaphthalene trisulfonic acid, naphthol sulfonic acid, dihydroxynaphthalene sulfonic acid, naphtholdisulfonic acid, aminonaphtholsulfonic acid, aminonaphtholdisulfonic acid, 1-(4'-amino-2'-chlorobenzoylamino)-8-naphthol-3,6-disulfonic acid, 1-(4'-nitrobenzene)amino-8-naphthol-3,6-disulfonic and nitronaphthol sulfonic acid, anthracene

5 sulfonic acid, anthraquinon sulfonic acid, anthraquinon disulfonic acid, aminoanthraquinon sulfonic acid, diaminoanthraquinon disulfonic acid, nitroanthraquinon sulfonic acid, dihydroanthraquinon sulfonic acid, diaminodioxanthraquinon sulfonic acid, diaminoanthraquinon disulfonic acid, bromoethane sulfonic acid, 3-fluoromethanesulfonic acid, perchlorooctane sulfonic acid, aminoethane sulfonic acid, hydroxyheptane sulfonic acid, dodecyloxybutane sulfonic acid, propargyloxypropyl sulfonic acid, acetone disulfonic acid, bis[octylsulfonic acid substituted]-sulfonic acid, -dihydroxyethane sulfonic acid, mercaptopropane sulfonic acid, methane sulfonic acid, and  $\alpha$ -olefine sulfonic acid.

Among the organic phosphoric acid or esters thereof include nitrilotrimethylphosphoric acid, aminodimethylphosphonomonoethylphosphoric acid, ethylenediaminethramethylphosphoric acid, diethlenetriaminepentamethylphosphoric acid, triethylenetetraminehexamethylphosphoric acid, hydroxyethylidenidiphosphoric acid, hydroxypropylidenediphosphoric acid, 1,2,4-tricarboxybutane-2-phosphoric acid, 1,2-dicarboxybutane-2-phosphoric acid, 1,2,4-tricarboxyhexane-1-phosphoric acid,  $\beta$ -chloroethylacidphosphate, bis[(2-hydroxyethyl)-methacrylate]acidphosphate, 2-ethylhexylacidphosphate, methylacidphosphate, ethylacidphosphate, propylacidphosphate, butylacidphosphate, octylacidphosphate, decylacidphosphate, laurylacidphosphate, stearylacidphosphate, dibutylacidphosphate, di-( $\beta$ -chloroethyl)acidphosphate, di(2-ethylhexyl)acidphosphate, dimethylacidphosphate, diethylacidphosphate, dipropylacidphosphate, dioctylacidphosphate, didecylacidphosphate, dilaurylacidphosphate, distearylacidphosphate, tributylphosphite, tris(2-ethylhexyl)phosphite, tridecylphosphite, tristearylphosphite, tris(nonylphenyl)phosphite, trisphenylphosphite, trislaurylthiophosphite, tris(2,3-dichloropropyl)phosphite, diphenyldecylphosphite, diphenyltridecylphosphite, trimethylphosphite, triethylphosphite, trioctylphosphite, trilaurylphosphite, dilaurylhydrogenphosphite, diphenylhydrogenphosphite, demethylhydrogenphosphite, diethylhydrogenphosphite, depropylhydrogenphosphite, dibutylhydrogenphosphite, dioctylhydrogenphosphite, didecylhydrogenphosphite, distearylhydrogenphosphite. These acid catalysts only named few, not limiting thereto.

25 The amount of acid catalyst to be used in the sizing agent is 0.0001 to 10.0 parts by weight, preferably 0.001 to 1 parts by weight of the acid catalyst per 100 parts by weight of the sizing agent.

The following Examples will illustrate the present invention, but limited thereto is not the scope of the invention

#### 30 Comparative Example 1

A sizing agent was prepared by mixing 10g of cationic starch with 90ml water, boiling the resulting mixture at 95-97 °C for 15 minutes and then adding 5g of dodecylsuccinic anhydride thereto.

#### 35 Comparative Example 2

A sizing agent was prepared similar to Comparative Example 1 except that octadecenylsuccinic anhydride acid was used in place of dodecylsuccinic anhydride.

#### 40 Comparative Example 3

A sizing agent was prepared by modifying the pH of a commercially available rosin based sizing agent to 4.5 with alum.

#### 45 Comparative Example 4

A sizing agent was prepared by adding cationized cellulose to a commercially available alkylketene dimer based sizing agent in an amount to 25 % by weight of the agent.

#### 50 Example 1

55 In a 4 necked flask 1 mole of dodecenylsuccinic anhydride and 1 mole of allyl alcohol were reacted together at 110  $\pm$  5 °C for 2 hours to form a monoallyl ester of dodecylsuccinic acid. The product thus obtained was then converted to its triethanolamine salt which is a viscous yellowish brown liquid having a good self-emulsifiability in water.

Similarly, monoesters hereinafter described were prepared and these monoesters were subjected to a sizing test in the form of amine salts, sodium salts or potassium salts and like.

60 The degree of sizing achieved by the above mentioned sizing agents was measured under conditions set forth below. The test results thus obtained are reproduced in Table 1 (succinic acid is abbreviated as s.a.). Each sizing agent was added to a 0.5% aqueous pulp slurry in an amounts of 0.05, 0.1 and 0.2 % by weight of the sizing agent (on the basis of pulp solid) and then mixed together for 15 minutes.

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The test conditions were as follows:

|                        |                                  |
|------------------------|----------------------------------|
| pulp concentration     | 0.5%                             |
| paper-making procedure | TAPPI STANDARD MACHINE           |
| basis weight           | 70 g/m <sup>2</sup>              |
| filler                 | heavy calcium carbonate          |
| drying                 | 110°C for 5 minutes              |
| sizing test            | JIS P8122 Stoechlitz sizing test |

Table 1

| Sample No.           | sizing agent   | degree of sizing wt. % added |     |     |
|----------------------|--|------------------------------|-----|-----|
|                      |  | 0.05                         | 0.1 | 0.2 |
| 1                    | Na salt of monoallylester of hexenyl-s.a.            | 12                           | 23  | 30  |
| 2                    | K salt of monopropargyl ester of octenyl-s.a.        | 11                           | 22  | 29  |
| 3                    | TEA salt of monooleyl ester of decenyl-s.a.          | 11                           | 21  | 29  |
| 4                    | TEA salt of monoallyl ester of dodecenyl-s.a.        | 12                           | 23  | 31  |
| 5                    | MEA salt of monobutenyl ester of octadecenyl-s.a.    | 11                           | 20  | 29  |
| 6                    | TEtA salt of monohexenyl ester of dodecenyl-s.a.     | 13                           | 23  | 30  |
| 7                    | MMtA salt of monolaurenyl ester of octenyl-s.a.      | 12                           | 22  | 28  |
| 8                    | TEA salt of monobutyl ester of octadecenyl-s.a.      | 11                           | 21  | 27  |
| 9                    | DEA salt of monopropargyl ester of dodecenyl-s.a.    | 13                           | 22  | 29  |
| 10                   | MEA salt of monoallyl ester of octadecenyl-s.a.      | 13                           | 23  | 30  |
| 11                   | MEA salt of monoallyl ester of eicocenyl-s.a.        | 11                           | 20  | 27  |
| 12                   | DEA salt of monopropargyl ester of tetracocenyl-s.a. | 11                           | 21  | 27  |
| 13                   | MEA salt of monobutenyl ester of triancotenyl-s.a.   | 12                           | 21  | 28  |
| 14                   | TEA salt of monopentenyl ester of tetracocenyl-s.a.  | 12                           | 20  | 27  |
| 15                   | TEtA salt of monooleyl ester of eicocenyl-s.a.       | 12                           | 20  | 28  |
| Comparative Examples |  |                              |     |     |
| 1                    | dodecenylsuccinic anhydride                          | 3                            | 9   | 14  |
| 2                    | octadecenylsuccinic anhydride                        | 4                            | 10  | 16  |
| 3                    | rosin based sizing agent                             | 9                            | 12  | 20  |
| 4                    | alkylketene dimer based sizing agent                 | 11                           | 20  | 26  |

Note:

TEA: triethanolamine; DEA: diethanolamine; MEA: monoethanolamine;

TEtA: triethylamine; MMtA: monomethylamine.

From the foregoing, it is clear that the sizing agents of the present invention have superior sizing effects over the conventional ones.

#### Example 2

Cationic starch (10g) was boiled with 90 ml of water at 95-97 °C for 15 minutes to which was added 5 g of the sizing agent set forth in Table 2 and resultant product was subjected to the sizing test as set forth in Example 1 in order to measure the degree of sizing achieved by the product. The results obtained are reproduced in Table 2 below.

Table 2

|    | Sample No.         | sizing agent                                      | degree of sizing wt. % added |     |     |
|----|--------------------|---|------------------------------|-----|-----|
|    |                    |   | 0.05                         | 0.1 | 0.2 |
| 5  | 16                 | monoallyl ester of dodecenyl-s.a.                 | 12                           | 24  | 35  |
|    | 17                 | monopropargyl ester of octadecenyl-s.a.           | 12                           | 22  | 32  |
|    | 18                 | monoallyl ester of elcocenyl-s.a.                 | 12                           | 21  | 30  |
| 10 | 19                 | monolaurenyl ester of octenyl-s.a.                | 12                           | 23  | 31  |
|    | 20                 | monooleyl ester of triancotenyl-s.a.              | 12                           | 22  | 30  |
|    | 21                 | TEA salt of monoallyl ester of dodecenyl-s.a.     | 13                           | 24  | 33  |
|    | 22                 | TEA salt of monopropargyl ester of octenyl-s.a.   | 13                           | 22  | 30  |
| 15 | 23                 | DEA salt of monopropargyl ester of dodecenyl-s.a. | 14                           | 23  | 32  |
|    | 24                 | MEA salt of monobutenyl ester of octadecenyl-s.a. | 13                           | 22  | 31  |
|    | Compative Examples |   |                              |     |     |
| 20 | 1                  | dodecenylsuccinic anhydride                       | 3                            | 9   | 14  |
|    | 2                  | octadecenylsuccinic anhydride                     | 4                            | 10  | 16  |

## 25 Comparative Example 5

A monoallylester of decenylsuccinic acid was prepared as in Example 3 hereinafter described and the resultant product was modified with cationic starch to form a homogeneous slurry.

## 30 Comparative Example 6

A monoallylester of octadecenylsuccinic acid was prepared as in Example 3 hereinafter described, but without addition of benzene sulfonic acid. The resultant monoallylester was mixed with cationic starch as in Comparative Example 1 to form a homogeneous slurry.

## 35 Example 3

A monoallylester of octadecenylsuccinic acid was sythesized by reacting in a three-necked flask 1 mole of octadecenylsuccinic anhydride and 1 mole of allylalccohol together at  $110 \pm 5$  °C for two hours. To the resultant monoallylester of octadecenylsuccinic acid was added 0.1% by weight of benzensulfonic acid on the basis of the weight of the monoallylester. The product thus obtained was modified with cationic starch as in Comparative Example 1 to form a homogeneuos slurry (sample No.25).

Similarly additional sizing agents were prepared as set forth in Table 3, in which cat. wt. % means the amount (on a weight percent of sizing agent basis) of the indicated catalyst added.

Each sizing agent produced in Example 3 and Comparative Examples 1 to 4 set forth above and Comparative Example 5 and 6 were added to a 0.5 % pulp slurry so as to provide sizing agent concentration of 0.05 %, 0.1 %, and 0.2 % on the basis of the pulp solid and then mixed together for 15 minutes. The resulting slurry was subjected to a sizing test. The results obtained are reproduced in Tables 3 and 4.

## 50 Sizing test conditions:

|               |  |
|---------------|--|
| Pulp:         | LBKP : NBKP = 1:1                          |
| CSF:          | 400  |
| paper-making  | TAPPI STANDARD MACHINE                     |
| basis weight  | 70 g/m <sup>2</sup>                        |
| filler        | heavy calcium carbonate                    |
| drying        | 110°C for 5 minutes                        |
| sizing degree | JIS P-8122 Stoechigt sizing test procedure |

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Table 3

| Sample No.           | sizing agent | cat. wt. %                              | degree of sizing wt. % added |     |      |
|----------------------|--------------|---|------------------------------|-----|------|
|                      |              |   | 0.05                         | 0.1 | 0.15 |
| 5                    | 25           | monoallylester of octadecenyl-s.a.      | benzenesulfonic acid         |     |      |
|                      |              | 0.1                                     | 18                           | 59  | 69   |
|                      | 28           | monoallylester of hexenyl-s.a.          | benzenesulfonic acid         |     |      |
|                      |              | 0.1                                     | 18                           | 48  | 59   |
| 10                   | 27           | monopropargylester of octenyl-s.a.      | naphthylsulfonic acid        |     |      |
|                      |              | 0.1                                     | 15                           | 42  | 51   |
|                      | 28           | monoallylester of decenyl-s.a.          | toluenesulfonic acid         |     |      |
|                      |              | 0.2                                     | 17                           | 54  | 63   |
| 15                   | 29           | monoallylester of dodecenyl-s.a.        | toluenesulfonic acid         |     |      |
|                      |              | 0.1                                     | 19                           | 61  | 72   |
|                      | 30           | monohexenylester of octadecenyl-s.a.    | butylbenzenesulfonic acid    |     |      |
|                      |              | 0.15                                    | 17                           | 58  | 66   |
| 20                   | 31           | monobutenylester of dodecenyl-s.a.      | methylnaphthylsulfonic acid  |     |      |
|                      |              | 0.1                                     | 16                           | 58  | 65   |
|                      | 32           | monoallylester of octadecenyl-s.a.      | ligninsulfonic acid          |     |      |
|                      |              | 0.1                                     | 21                           | 66  | 75   |
| 25                   | 33           | monopentenylester of octenyl-s.a.       | phosphoric acid              |     |      |
|                      |              | 0.1                                     | 14                           | 41  | 50   |
|                      | 34           | monodecenylester of dodecenyl-s.a.      | zinc chloride                |     |      |
|                      |              | 0.15                                    | 14                           | 42  | 53   |
| 30                   | 35           | monooleylester of dococenyl-s.a.        | ferric chloride              |     |      |
|                      |              | 0.15                                    | 15                           | 46  | 55   |
|                      | 36           | monobutenylester of triancotenyl-s.a.   | benzenesulfonic acid         |     |      |
|                      |              | 0.15                                    | 16                           | 51  | 60   |
| 35                   | 37           | monobutynester of eicocenyl-s.a.        | diethylbenzenesulfonic acid  |     |      |
|                      |              | 0.05                                    | 13                           | 39  | 48   |
|                      | 38           | monolaurenylester of octadecenyl-s.a.   | toluenesulfonic acid         |     |      |
|                      |              | 0.2                                     | 18                           | 60  | 71   |
| 40                   | 39           | monooctenylester of eicocenyl-s.a.      | aluminium chloride           |     |      |
|                      |              | 0.3                                     | 17                           | 56  | 63   |
|                      | 40           | monopropargylester of hexenyl-s.a.      | propylnaphthylsulfonic acid  |     |      |
|                      |              | 0.05                                    | 14                           | 40  | 50   |
| 45                   | 41           | monobutynester of dodecenyl-s.a.        | sulfuric acid                |     |      |
|                      |              | 0.5                                     | 13                           | 36  | 43   |
|                      | 42           | monoallylester of octenyl-s.a.          | toluenesulfonic acid         |     |      |
|                      |              | 0.15                                    | 20                           | 63  | 72   |
| 50                   | 43           | monopropargylester of triancotenyl-s.a. | ligninsulfonic acid          |     |      |
|                      |              | 0.1                                     | 13                           | 40  | 50   |
|                      | 44           | monoallylester of octadecenyl-s.a.      | phosphoric acid              |     |      |
|                      |              | 0.1                                     | 16                           | 54  | 64   |
| Comparative Examples |              |   |                              |     |      |
| 55                   | 1            | dodecenylsuccinic anhydride             | phosphoric acid              |     |      |
|                      |              | 0.1                                     | 6                            | 15  | 21   |
|                      | 2            | octadecenyl succinic anhydride          | phosphoric acid              |     |      |
|                      |              | 0.1                                     | 7                            | 18  | 26   |
| 60                   | 3            | rosin based sizing agent                | —                            | 10  | 20   |
|                      | 4            | alkylketene dimer based sizing agent    | —                            | 11  | 27   |
|                      | 5            | monoallylester of dodecenyl-s.a.        | —                            | 13  | 35   |
|                      | 6            | monoallylester of octadecenyl-s.a.      | —                            | 16  | 34   |

Table 4

| Sample No. | sizing agent | Cat. wt. %                            | degree of sizing wt. % added          |     |     |
|------------|--------------|---------------------------------------|---------------------------------------|-----|-----|
|            |              |                                       | 0.05                                  | 0.1 | 0.2 |
| 5          | 45           | monopropargylester of hexenyl-s.a.    | bromoethanesulfonic acid              |     |     |
|            |              |                                       | 0.1                                   | 12  | 32  |
|            | 46           | monobutenylester of octenyl-s.a.      | perchlorooctanesulfonic acid          |     |     |
|            |              |                                       | 0.1                                   | 12  | 31  |
| 10         | 47           | monoallylester of decenyl-s.a.        | aminoethanesulfonic acid              |     |     |
|            |              |                                       | 0.15                                  | 11  | 29  |
|            | 48           | monooleylester of dodecenyl-s.a.      | hydroxyheptanesulfonic acid           |     |     |
|            |              |                                       | 0.15                                  | 11  | 30  |
| 15         | 49           | monopentenylester of octadecenyl-s.a. | dodecyloxypropylsulfonic acid         |     |     |
|            |              |                                       | 0.2                                   | 12  | 34  |
|            | 50           | monoallylester of elcocenyl-s.a.      | acetonedisulfonic acid                |     |     |
|            |              |                                       | 0.05                                  | 11  | 31  |
| 20         | 51           | monohexenylester of triacontenyl-s.a. | dioctylsulfonic acid-substituted-s.a. |     |     |
|            |              |                                       | 0.15                                  | 12  | 33  |
|            | 52           | monopropargylester of dodecenyl-s.a.  | mercaptopropanesulfonic acid          |     |     |
|            |              |                                       | 0.2                                   | 12  | 33  |
| 25         | 53           | monoallylester of octadecenyl-s.a.    | methanesulfonic acid                  |     |     |
|            |              |                                       | 0.1                                   | 11  | 30  |
|            | 54           | monoallylester of octenyl-s.a.        | dichlorobenzenesulfonic acid          |     |     |
|            |              |                                       | 0.15                                  | 13  | 36  |
| 30         | 55           | monopropargylester of decenyl-s.a.    | dichlorotoluenesulfonic acid          |     |     |
|            |              |                                       | 0.15                                  | 13  | 35  |
|            | 56           | monooleylester of hexenyl-s.a.        | aminotoluenesulfonic acid             |     |     |
|            |              |                                       | 0.2                                   | 14  | 40  |
| 35         | 57           | monolaurenylester of dodecenyl-s.a.   | notrobenzensulfonic acid              |     |     |
|            |              |                                       | 0.1                                   | 16  | 43  |
|            | 58           | monobutenylester of octadecenyl-s.a.  | dinitromethylenesulfonic acid         |     |     |
|            |              |                                       | 0.1                                   | 15  | 43  |
| 40         | 59           | monobutenylester of dococenyl-s.a.    | nitrochlorobenzenesulfonic acid       |     |     |
|            |              |                                       | 0.15                                  | 13  | 37  |
|            | 60           | monohexenylester of decenyl-s.a.      | dinitrochlorobenzenesulfonic acid     |     |     |
|            |              |                                       | 0.15                                  | 15  | 41  |
| 45         | 61           | monoallylester of triacontenyl-s.a.   | phenolsulfonic acid                   |     |     |
|            |              |                                       | 0.2                                   | 18  | 55  |
|            | 62           | monopropargylester of octenyl-s.a.    | cresolsulfonic acid                   |     |     |
|            |              |                                       | 0.2                                   | 14  | 37  |
| 50         | 63           | monoallylester of dodecenyl-s.a.      | naphthalenedisulfonic acid            |     |     |
|            |              |                                       | 0.05                                  | 20  | 60  |
|            | 64           | monopentenylester of elcocenyl-s.a.   | naphthalenetrisulfonic acid           |     |     |
|            |              |                                       | 0.05                                  | 19  | 58  |
| 55         | 65           | monooleylester of octadecenyl-s.a.    | nitronaphthalenedisulfonic acid       |     |     |
|            |              |                                       | 0.05                                  | 17  | 56  |
|            | 66           | monoallylester of octadecenyl-s.a.    | naphtholsulfonic acid                 |     |     |
|            |              |                                       | 0.1                                   | 21  | 61  |
| 60         | 67           | monoallylester of dodecenyl-s.a.      | aminonaphtholsulfonic acid            |     |     |
|            |              |                                       | 0.1                                   | 18  | 59  |
|            | 68           | monohexenylester of dococenyl-s.a.    | anthracenesulfonic acid               |     |     |
|            |              |                                       | 0.15                                  | 17  | 55  |

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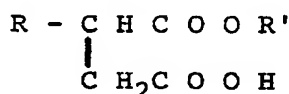
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| Sample No. | sizing agent                               | Cat. wt. %                                      | degree of sizing wt. % added |     |     |
|------------|--|---|------------------------------|-----|-----|
|            |  |   | 0.05                         | 0.1 | 0.2 |
| 5          | 69 monooctenylester of hexenyl-s.a.        | anthraquinonesulfonic acid                      |                              |     |     |
|            |  | 0.15  | 17                           | 54  | 72  |
|            | 70 monooleylester of octenyl-s.a.          | anthraquinonedisulfonic acid                    |                              |     |     |
|            |  | 0.1   | 19                           | 59  | 79  |
| 10         | 71 monobutenylester of eicosenyl-s.a.      | aminoanthraquinonesulfonic acid                 |                              |     |     |
|            |  | 0.15  | 14                           | 38  | 52  |
|            | 72 monopropargylester of triacontenyl-s.a. | nitroanthraquinonesulfonic acid                 |                              |     |     |
|            |  | 0.1   | 15                           | 39  | 55  |
| 15         | 73 monoallylester of dodecenyl-s.a.        | hydroxyethylidenediphosphoric acid              |                              |     |     |
|            |  | 0.2   | 22                           | 65  | 76  |
|            | 74 monoallylester of octadecenyl-s.a.      | 1,2,4-tricarboxybutane-2-phosphoric acid        |                              |     |     |
|            |  | 0.1   | 20                           | 63  | 75  |
| 20         | 75 monopropargylester of octenyl-s.a.      | 1,2-dicarboxybutane-2-phosphoric acid           |                              |     |     |
|            |  | 0.2   | 19                           | 60  | 72  |
|            | 76 monooleylester of decenyl-s.a.          | nitrotrimethylphosphoric acid                   |                              |     |     |
|            |  | 0.1   | 16                           | 59  | 72  |
| 25         | 77 monobutenylester of hexenyl-s.a.        | hydroxypropylidenediphosphoric acid             |                              |     |     |
|            |  | 0.2   | 21                           | 63  | 74  |
|            | 78 monoallylester of triacontenyl-s.a.     | triethylenetetraminehexamethyl-phosphoric acid  |                              |     |     |
|            |  | 0.2   | 17                           | 58  | 70  |
| 30         | 79 monopropargylester of octadecenyl-s.a.  | phosphorous acid                                |                              |     |     |
|            |  | 0.15  | 12                           | 55  | 65  |
|            | 80 monopropargylester of dodecenyl-s.a.    | hypophosphorous acid                            |                              |     |     |
|            |  | 0.15  | 14                           | 53  | 64  |
| 35         | 81 monoallylester of dodecenyl-s.a.        | 2-ethylhexylacidphosphate                       |                              |     |     |
|            |  | 0.1   | 22                           | 66  | 77  |
|            | 82 monoallylester of octadecenyl-s.a.      | butylacidphosphate                              |                              |     |     |
|            |  | 0.1   | 23                           | 67  | 79  |
| 40         | 83 monopropargylester of decenyl-s.a.      | $\beta$ -chloroethylacidphosphate               |                              |     |     |
|            |  | 0.15  | 21                           | 64  | 74  |
|            | 84 monooleylester of hexenyl-s.a.          | bis[(2-hydroxyethyl)methacrylate]-acidphosphate |                              |     |     |
|            |  | 0.15  | 20                           | 63  | 72  |
| 45         | 85 monopropargylester of dodecenyl-s.a.    | laurylacidphosphate                             |                              |     |     |
|            |  | 0.15  | 21                           | 65  | 74  |
|            | 86 monoallylester of octadecenyl-s.a.      | dibutylacidphosphate                            |                              |     |     |
|            |  | 0.1   | 24                           | 65  | 78  |
| 50         | 87 monooleylester of hexenyl-s.a.          | distearylacidphosphate                          |                              |     |     |
|            |  | 0.15  | 22                           | 64  | 73  |
|            | 88 monoallylester of dodecenyl-s.a.        | di(2-ethylhexyl)acidphosphate                   |                              |     |     |
|            |  | 0.15  | 21                           | 67  | 78  |
| 55         | 89 monopropargylester of decenyl-s.a.      | di( $\beta$ -chloroethyl)acidphosphate          |                              |     |     |
|            |  | 0.2   | 21                           | 65  | 75  |
|            | 90 monobutenylester of dodecenyl-s.a.      | dioctylacidphosphate                            |                              |     |     |
|            |  | 0.1   | 22                           | 63  | 74  |
| 60         | 91 monohexenylester of triacontenyl-s.a.   | tributylphosphite                               |                              |     |     |
|            |  | 0.2   | 17                           | 52  | 70  |
|            | 92 monopentenylester of octenyl-s.a.       | tristearylphosphite                             |                              |     |     |
|            |  | 0.2   | 15                           | 41  | 68  |
| 65         | 93 monooleylester of eicosenyl-s.a.        | tris(2,3-dichloropropyl)phosphite               |                              |     |     |
|            |  | 0.15  | 14                           | 40  | 66  |

| Sample No. | sizing agent                          | Cat. wt. %                | degree of sizing wt. % added |     |     |
|------------|---------------------------------------|---------------------------|------------------------------|-----|-----|
|            |                                       |                           | 0.05                         | 0.1 | 0.2 |
| 94         | monobuthenylester of octadecenyl-s.a. | diphenyldecylphosphite    | 0.15                         | 16  | 51  |
| 95         | monopropargylester of dodecenyl-s.a.  | diphenylhydrogenphosphite | 0.2                          | 13  | 39  |
|            |                                       |                           |                              |     | 62  |

### Claims

1. A method of sizing paper utilizing as a sizing agent a composition comprising one or more partial esters of alkenylsuccinic acids represented by the formula:

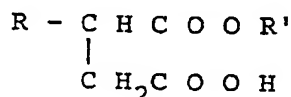


and/or one or more salts thereof, wherein R represents an unsaturated hydrocarbyl group having at least 6 carbon atoms and R' represents an unsaturated hydrocarbyl group having 3 to 18 carbon atoms.

2. A method as claimed in claim 1 wherein said salt is selected from a water soluble amine salt and/or an alkaline metal salt.
3. A method as claimed in claim 1 wherein an acid catalyst is further included therein.
4. A method as claimed in claim 3 wherein said catalyst is selected from a sulfonic acid, an organic phosphoric acid, an inorganic acid, or Lewis acid.
5. A method as claimed in claim 4 wherein said inorganic acid is selected from phosphoric acid, phosphorous acid, hypophosphorous acid, sulfuric acid, hydrochloric acid or nitric acid.
6. A method as claimed in claim 4 wherein said Lewis acid is selected from boron fluoride, zinc chloride, aluminium chloride, or ferric chloride.

### Patentansprüche

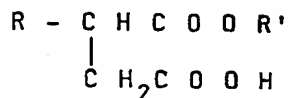
1. Verfahren zum Schichten von Papier unter Verwendung einer Zusammensetzung als Schlichtmittel, die einen oder mehrere Teilester von Alkenylbernsteinsäure der Formel



- und/oder ein oder mehrere Salze davon umfaßt, wobei R einen ungesättigten Kohlenwasserstoffrest mit mindestens 6 Kohlenstoffatomen und R' einen ungesättigten Kohlenwasserstoffrest mit 3 bis 18 Kohlenstoffatomen darstellt.
2. Verfahren nach Anspruch 1, wobei das Salz aus einem wasserlöslichen Aminsatz und/oder einem Alkalimetallsatz ausgewählt ist.
3. Verfahren nach Anspruch 1, wobei ferner ein saurer Katalysator enthalten ist.
4. Verfahren nach Anspruch 3, wobei der Katalysator aus einer Sulfonsäure, einer organischen Phosphorsäure, einer anorganischen Säure oder einer Lewis-Säure ausgewählt ist.
5. Verfahren nach Anspruch 4, wobei die anorganische Säure aus Phosphorsäure, phosphoriger Säure, hypophosphoriger Säure, Schwefelsäure, Salzsäure oder Salpetersäure gewählt ist.
6. Verfahren nach Anspruch 4, wobei die Lewis-Säure aus Borfluorid, Zinkchlorid, Aluminiumchlorid oder Eisen(III)-chlorid gewählt ist.

### Revendications

1. Méthode pour l'encollage du papier en utilisant comme agent d'encollage une composition comprenant un ou plusieurs esters partiels d'acides alkenylsucciniques représentés par la formule:



- 5 et/ou un ou plusieurs sels de ceux-ci, où R représente un groupe hydrocarbyle insaturé ayant au moins 6 atomes de carbone et R' représente un groupe hydrocarbyle insaturé ayant 3 à 18 atomes de carbone.
2. Méthode selon la revendication 1, où ledit sel est choisi parmi un sel d'amine soluble dans l'eau et/ou un sel d'un métal alcalin.
- 10 3. Méthode selon la revendication 1, où un catalyseur acide y est de plus incorporé.
4. Méthode selon la revendication 3, où ledit catalyseur est choisi parmi un acide sulfonique, un acide phosphorique, un acide inorganique ou un acide de Lewis.
5. Méthode selon la revendication 4, où ledit acide inorganique est choisi parmi l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux, l'acide sulfurique, l'acide chlorhydrique ou l'acide nitrique.
- 15 6. Méthode selon la revendication 4, où ledit acide de Lewis est choisi parmi le fluorure de bore, le chlorure de zinc, le chlorure d'aluminium ou le chlorure ferrique.

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